

(19) World Intellectual Property
Organization
International Bureau



532,615
25 APR 2005

(43) International Publication Date
6 May 2004 (06.05.2004)

PCT

(10) International Publication Number
WO 2004/038827 A2

- (51) International Patent Classification⁷: **H01M**
- (21) International Application Number:
PCT/US2003/033810
- (22) International Filing Date: 23 October 2003 (23.10.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/420,542 23 October 2002 (23.10.2002) US
- (71) Applicant (for all designated States except US): **IN-VENTQJAYA SDN. BHD.** [MY/MY]; Level 7, Setia 1, 15, Lorong Dungun, Damansara Heights, 50490, Kuala Lumpur (MY).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **MORRIS, William, F.** [US/US]; 2108 Central Park Avenue, Yonkers, NY 10710 (US). **SOLORZANO, Julio, G.** [US/US]; 2409 Mica Mine lane, Wake Forest, NC 27587 (US).
- (74) Agent: **CRISPINO, Ralph**; InventQjaya Sdn. Bhd., c/o Reveo Inc., 85 Executive Blvd., Elmsford, NY 10523 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— without international search report and to be republished upon receipt of that report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: LIQUID SEAL AND ELECTRICAL CONNECTION STRUCTURE

(57) Abstract: A metal air cell system is provided, generally wherein a common structure is used to electrically connect anodes and cathodes, and provide a sealed structure preventing liquid electrolyte leakage. A mechanism is provided which provides a downward force on an anode holder, pressing it onto a top plate of a base unit or cathode module. This downward force serves two purposes. First, a pressure is provided for a facial seal between the anode holder and the cathode module. This seal contains the electrolyte in the cathode module. Further, the interconnections are designed in such a way that allows this same downward force to provide a low resistance connection between anodes and cathodes.

WO 2004/038827 A2

Liquid Seal and Electrical Connection Structure

by William Morris and Julio Solorzano

BACKGROUND

Metal air electrochemical cells are desirable energy sources, particularly for features such as relatively high specific energy (W-H/kg). In general, metal electrode materials (anodes) are oxidized by hydroxide ions formed at an air diffusion electrode (cathode).

A typical metal air cell provides for electrical connection between cathodes and anodes by external current collectors. Further, many of electrochemical cells require the presence of a liquid electrolyte, which must preferably be contained to prevent spillage.

Various systems have been used for electrically interconnecting metal air electrochemical cells. Further, various systems have been used for sealing the liquid electrolyte contained within the metal air electrochemical cell system. However, these interconnection systems and sealing systems are oftentimes unrelated, and accordingly there is an increase in volume, complexity of system components, and overall weight. Further, time required to access, service and/or replace cells or components of such systems must account for overcoming both the interconnection systems and sealing systems. In the field of refuelable metal air electrochemical cells, ease of cell or component access, service and/or replacement cells is very important, indeed essential, to consumer acceptable and long lasting systems.

Accordingly, it would be desirable to have a metal air electrochemical cell system that includes convenient sealing and electrical interconnection systems.

SUMMARY

The above-discussed and other problems and deficiencies of the prior art are overcome or alleviated by the several methods and apparatus of the present invention. A metal air cell system is provided, generally wherein a common structure is used to electrically connect anodes and cathodes, and provide a sealed structure preventing liquid electrolyte leakage. A mechanism is provided which provides a downward force on an anode holder, pressing it onto a top plate of a base unit or cathode module. This downward force serves two purposes. First, a pressure is provided for a seal between the anode holder and the cathode module. This seal contains the electrolyte in the cathode module. Further, the interconnections provide a low resistance connection between anodes and cathodes.

The above-discussed and other features and advantages of the present invention will be appreciated and understood by those skilled in the art from the following detailed description and drawings.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a general schematic of a metal air cell system showing a set of anodes supported in an anode holder and a corresponding base unit;

Figure 2A shows the anodes inserted in the cathode structure and a contact cover of the base unit in the open position;

Figure 2B shows the contact cover of the base unit closed; and

Figure 3 details the electrical connection;

Figure 4A shows the springs locks and external connection terminals.

Figure 4B shows the anodes inserted in the cathode structure and a contact cover of the base unit in the open position;

Figure 4C shows a magnified view of the anodes inserted in the cathode structure and a contact cover of the base unit in the open position;

Figure 4D shows the posterior view of the contact cover of the base unit in the open position.

DESCRIPTION

Figures 1-4D generally show a system that allows for a common structure to electrically connect anodes and cathodes and provide a liquid electrolyte seal. Generally, a system 100 includes a base unit or structure 110 having one or more cathode structures 112 corresponding to anode receiving compartments 114 therein; an interconnect/seal cover or sealing connection structure 120; and a set of anodes 140.

Referring to Figure 1, the base unit 110 generally comprises one or more anode receiving structures 114. Each anode receiving structure 114 may include one or more air cathode structures 114 therein. Each anode compartment 114 is formed so as to contain a quantity of liquid electrolyte suitable for electrochemical reaction. Further, in a preferred embodiment, access openings 116 are provided on a side of the base 110 to allow air to access the air cathodes 114. Details of this structure are described, for example, in PCT Application Serial No. US03/00473 entitled "Reserve Battery" filed on January 8, 2003, and PCT Application Serial No. US/02/305585 entitled "Rechargeable and Refuelable Electrochemical Cell" filed on September 26, 2002, both of which are incorporated by reference herein in their entireties. Further, techniques for assembling plural cells to form a multiple cell system are described in PCT Application Serial No.

US03/00473 entitled "Reserve Battery" filed on January 8, 2003 and PCT Application Serial No. US03/17356 entitled "Method Of Manufacturing Metal Air Cell System" filed on June 2, 2003, both of which are incorporated by reference herein.

As is known in the art of metal air electrochemical cells, the metal anode may comprise suitable oxidizable metals such as magnesium, zinc, aluminum, calcium, lithium, ferrous metals, and combinations and alloys comprising at least one of the foregoing metals. During conversion in the electrochemical process, the metal is generally converted to a metal oxide. The anode may be in the form of a solid metal plate, or a structure of metal particles formed contiguously with suitable binders and the like.

The electrolyte generally comprises ion conducting liquid media. In a preferred embodiment, wherein the cell system is a magnesium air electrochemical cell, a neutral electrolyte such as salt water is used. However, caustic electrolytes may be used, e.g., potassium hydroxide, in zinc air or aluminum air system.

The air cathode may be a conventional air diffusion cathode, for example generally comprising an active constituent and a carbon substrate, along with suitable connecting structures, such as a current collector. The carbon used is preferably chemically inert to the electrochemical cell environment and may be provided in various forms including, but not limited to, carbon flake, graphite, other high surface area carbon materials, or combinations comprising at least one of the foregoing carbon forms. A binder is also typically used in the cathode, which may be any material that adheres substrate materials, the current collector, and the catalyst to form a suitable structure. An exemplary air cathode is disclosed in U.S. Patent No. 6,368,751, entitled

“Electrochemical Electrode For Fuel Cell”, to Wayne Yao and Tsepin Tsai, which is incorporated herein by reference in its entirety. Other air cathodes may instead be used, however, depending on the performance capabilities thereof, as will be obvious to those of skill in the art.

To electrically isolate the anode from the cathode, a separator is generally provided between the electrodes. The separator may be disposed in physical and ionic contact with at least a portion of at least one major surface of the anode, or all major surfaces of the anode, to form an anode assembly. In still further embodiments, the separator is disposed in physical and ionic contact with substantially the surface(s) of the cathode that will be proximate the anode. The physical and ionic contact between the separator and the anode may be accomplished by: direct application of the separator on one or more major surfaces of the anode; enveloping the anode with the separator; use of a frame or other structure for structural support of the anode, wherein the separator is attached to the anode within the frame or other structure; or the separator may be attached to a frame or other structure, wherein the anode is disposed within the frame or other structure.

The separator may be any commercially available separator capable of electrically isolating the anode and the cathode, while allowing sufficient ionic transport between the anode and the cathode, and maintaining mechanical integrity in the cell environment. Preferably, the separator is flexible, to accommodate electrochemical expansion and contraction of the cell components, and chemically inert to the cell chemicals. Suitable separators are provided in forms including, but not limited to, woven, non-woven, porous (such as microporous or nanoporous), cellular, polymer sheets, and the like. Materials

for the separator include, but are not limited to, polyolefin (e.g., Gelgard® commercially available from Dow Chemical Company), polyvinyl alcohol (PVA), cellulose (e.g., nitrocellulose, cellulose acetate, and the like), polyethylene, polyamide (e.g., nylon), fluorocarbon-type resins (e.g., the Nafion® family of resins which have sulfonic acid group functionality, commercially available from du Pont), cellophane, filter paper, and combinations comprising at least one of the foregoing materials. The separator may also comprise additives and/or coatings such as acrylic compounds and the like to make them more wettable and permeable to the electrolyte.

The anode set 140 generally includes one or more anodes in the form of a card structure. In one embodiment each of these anodes may comprise a plate 142 of an oxidizable metal material. In one preferred embodiment this metal material comprises magnesium. Where plurality of anode plates 142 are provided, a common support structure 144 is optionally provided for ease of replacement of the anode set 140. Optionally, the support structure 144 may serve as a gasket to prevent electrolyte from escaping the anode receiving structures 114. A top portion 146 of each anode plate extends through the structure 144. In one embodiment, as depicted, for magnesium cells, for example, this top portion 146 is the top of the anode plate 142 itself, thus, no external fasteners, wires, or other current collecting structures are required to be permanently attached to each anode plate 142. However, it is understood that, for example, in a zinc-air system, a current collector may be used and protrude through the anode holding plate.

The interconnect/seal structure 120 is shown in Figures 1 and 2A as being hingedly secured to the base 110 (e.g., with one or more suitable hinge structures); however, it is understood that the interconnect/seal structure 120 may be completely

detachable from the base 110. A set of electrical leads 122 extend from each cathode 114 into the connect/seal structure 120 (which is also described in the above cited references, particularly PCT Application Serial No. US03/00473 entitled "Reserve Battery" filed on January 8, 2003). These leads 122 through the connect/seal structure 120 provide operable electrical connection with corresponding anode connection terminals or contacts 124. The anode contacts 124 are positioned and dimensioned to mate with the top portions 146 of the anodes 142 when the anode set 140 is inserted within the base 110 and the cover 120 is closed (see detail in Figure 3). The anode contact may be any suitable electrical conducting structure. Preferably, this contact is resilient, such as a spring contact. The contacts 124 may be supported by the connect/seal structure 120 at plural ends (e.g., as depicted in Figures 1 and 2A), or by one end.

A locking structure or mechanism 128 may be provided at one side of the connect/seal cover 120 (e.g., wherein hinges are used on the opposing side), however, it is understood that a pair of locking structures may be used to secure the cover 120 to the base 110 (e.g., where no hinges are used). Other locking mechanisms may also be provided, as may become apparent to those skilled in the mechanical arts, for example, mating the connect/seal structure 120 with inside portions of the frame or case for the assembly. As depicted in Figures 2A and 2B, locking structure 128 mates with a corresponding protrusion 129 on the base 110.

For example, in one embodiment, and referring now to Figures 4A-4D, spring locks 130 may be provided on the connect/seal structure 120 that engage slots 132 of the side walls of the base unit 110 (e.g., where the side walls extent at least to the level of the connect/seal structure 120). Further, extending from each cathode 114 is a set of

electrical leads 122 whereby each lead is connected to traces or circuit line 121; wherein each traces 121 is mounted within an insulated circuit board 123. The insulated circuit board 123 is generally integral with the connect/seal structure 120. These leads 122 through the connect/seal structure 120 provide operable electrical connection with corresponding anode connection terminals or contacts 124.

One of the key advantages of the system described herein is that in order to remove the complete anode set 140, no mechanical force is required to overcome the electrical interconnections, since the anode set 140 is positioned within the base 110 with no mechanical resistance from the interconnects. In one known metal air refuelable system, a mechanical locking structure is used to secure the anodes into the anode receiving structures for example, in PCT/US00/28185 filed on 10/12/2000 entitled "Fuel Cell Support and Electrical Interconnector", incorporated by reference herein. The anode current collector extends from the anode structure and is electrically and mechanically connected with a cathode terminal; therefore to remove the anode, the force of the current collector and terminal interaction must be overcome.

On the other hand, with the system of the present invention, the force that secures the anode set 140 is the locking force, e.g., of the mechanism(s) 128 in the depicted embodiment of Figures 2A-3, and 130 in Figures 4A-4D. When the force is released, the anode set 140 is also released both electrically and mechanically.

When liquid electrolyte is introduced into each of the receiving structures 114, it is desirable to have a structure that prevents electrolyte from leaking out of the receiving structures, particularly when the anode set 140 is in place. In a preferred embodiment this is accomplished by utilizing an elastomeric material for the anode support structure

144. Accordingly, the top of the base structure 110 and the underside of the interconnect/seal cover 120 are configured and dimensioned to tightly receive this elastomeric material providing a gasket seal. In addition to preventing liquid from escaping the receiving structures 114, this seal also serves to prevent any liquid between the connection of the top portion 146 of the anode 142 and the anode terminal 124 on the underside of the cover 120.

Another beneficial feature of the system of the present invention is that external connections terminals as depicted in embodiment 4A may be provided at the top of the structure 120, as opposed to a separate interconnect which is commonly used when replaceable anodes are used.

Various materials may be used for the cell frame components, spacers, locking mechanisms or structures, and other support structures described herein, which are preferably inert to the system chemicals. Such materials include, but not limited to, thermoset, thermoplastic, and rubber materials such as polycarbonate, polypropylene, polyetherimide, polysulfonate, polyethersulfonate, polyarylether ketone, Viton® (commercially available from EI DuPont de Nemours & Co., Wilmington Delaware), Delrin® (commercially available from EI DuPont de Nemours & Co., Wilmington Delaware), ethylenepropylenediene monomer, ethylenepropylene rubber, and mixtures comprising at least one of the foregoing materials.

While preferred embodiments have been shown and described, various modifications and substitutions may be made thereto without departing from the spirit and scope of the invention. Accordingly, it is to be understood that the present invention has been described by way of illustrations and not limitation.

Claims:

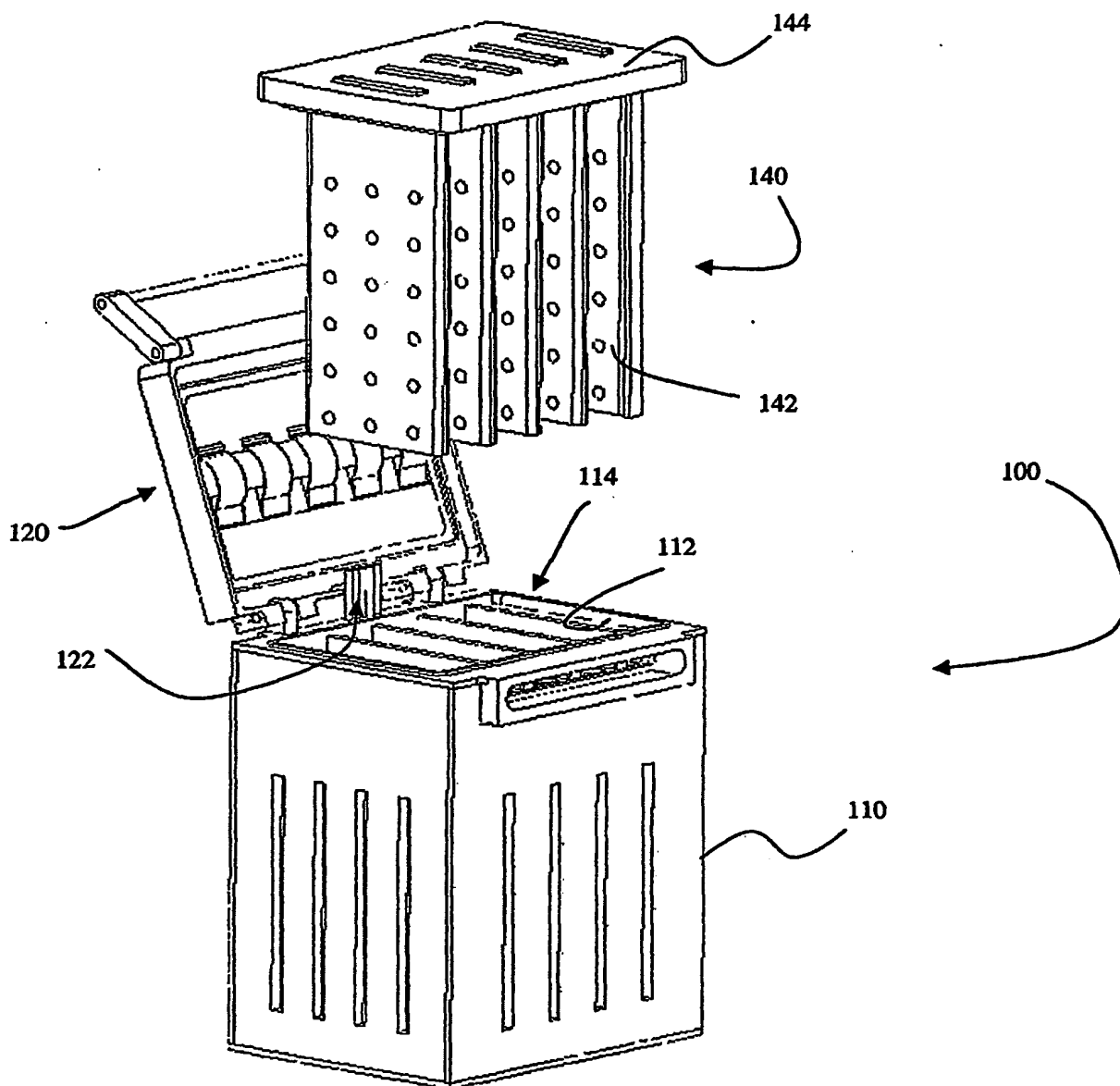
1. A metal air electrochemical cell comprising:
 - a base structure having
 - one or more anode receiving structures supported therein, said anode-receiving structure including an air cathode having air access;
 - a sealing/connection structure including an anode connection terminal on a side thereof corresponding to an open end of the anode receiving structure,
 - wherein the air cathode in the base structure is electrically connected to the anode connection terminal with a connection allowing the sealing/connection structure to be partially or completely displaced from the base structure, and
 - at least one anode card for insertion into the anode receiving structure,wherein the cell is placed into a discharging mode by closing the sealing/connection structure such that the anode connection terminal electrically connects the anode card.
2. The metal air electrochemical cell as in claim 1, wherein the anode receiving structure is formed so as to maintain a quantity of liquid electrolyte, wherein said sealing/connection structure connects to said base structure for both electrical connection and for sealing.
3. The metal air electrochemical cell as in claim 2, comprising a plurality of anode receiving structures, wherein a plurality of anode supporting cards are supported by an anode support structure.

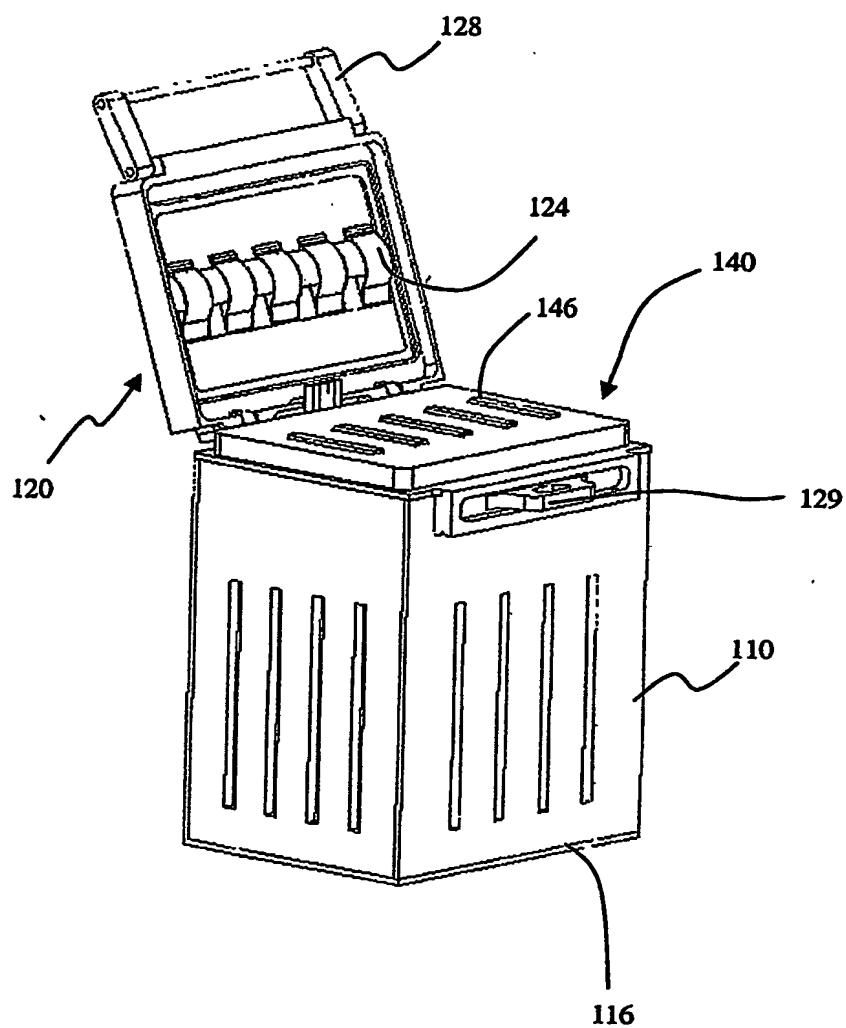
4. The metal air electrochemical cell as in claim 3, wherein the anode support structure forms a gasket between the base and the top cover.
5. The metal air electrochemical cell as in claim 4 wherein the gasket prevents liquid from accessing the connection between the anode card and the anode connection terminal.
6. The metal air electrochemical cell as in claim 1, wherein the anode card includes a contiguous end positioned as an electrical contact point with the anode connection terminal in the discharging mode.
7. The metal air electrochemical cell as in claim 6, wherein the anode card comprises magnesium or magnesium alloys.
8. The metal air electrochemical cell as in claim 1, wherein the anode card includes an anode current collector as an electrical contact point with the anode connection terminal in the discharging mode.
9. The metal air electrochemical cell as in claim 8, wherein the anode card comprises zinc or zinc alloys.
10. The metal air electrochemical cell as in claim 1, wherein the connection allowing the sealing/connection structure to be displaced from the base structure comprises a

flexible electrical connection, and further wherein the base structure and the sealing/connection structure are connected by a hinge structure.

11. The metal air electrochemical cell as in claim 1, wherein the connection allowing the sealing/connection structure to be displaced from the base structure comprises a removable electrical connection.
12. The metal air electrochemical cell as in claim 1, wherein the sealing/connection structure includes a locking mechanism corresponding to a receiving structure on the base structure.
13. The metal air electrochemical cell as in claim 12, wherein the locking mechanism comprises a latch corresponding to a receiving structure comprising a protrusion.
14. The metal air electrochemical cell as in claim 12, wherein the locking mechanism comprises a spring lever corresponding to a receiving structure comprising a slot or aperture.
15. The metal air electrochemical cell as in claim 1, wherein the base structure includes a locking mechanism corresponding to a receiving structure on the sealing/connection structure.

16. The metal air electrochemical cell as in claim 15, wherein the locking mechanism comprises a latch corresponding to a receiving structure comprising a protrusion.
17. The metal air electrochemical cell as in claim 15, wherein the locking mechanism comprises a spring lever corresponding to a receiving structure comprising a slot or aperture.
18. The metal air electrochemical cell as in claim 1, the base structure including apertures for allowing air to access the air cathode.
19. The metal air electrochemical cell as in claim 1, wherein the anode connection terminal comprises a flexible conductor supported by the sealing/connection structure.
20. A method of operating a metal air electrical cell system comprising
inserting an anode card into an anode receiving structure within a base, the anode receiving structure having an air cathode integral therein accessing air;
placing a top cover having an anode terminal and a flexible electrical connection with the air cathode over the base so as to electrically connect the anode terminal and the anode card, and to mechanically secure the anode card;
discharging the anode to a desired level of discharge (e.g., until output drops below a certain voltage level).
21. The method of claim 20, further comprising removing the cover from the base thereby releasing electrical contact with the anode.

**FIGURE 1**

**FIGURE 2A**

SUBSTITUTE SHEET (RULE 26)

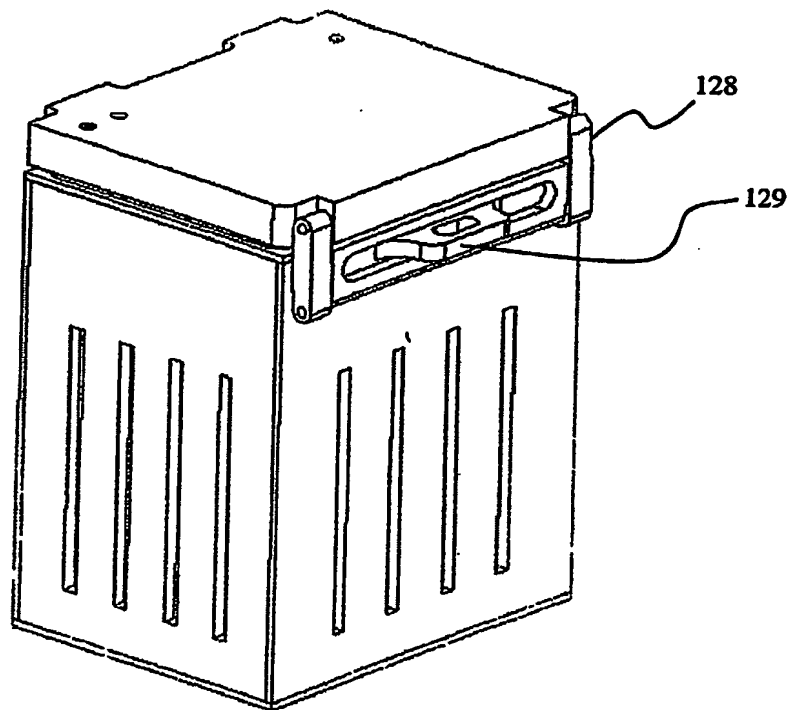
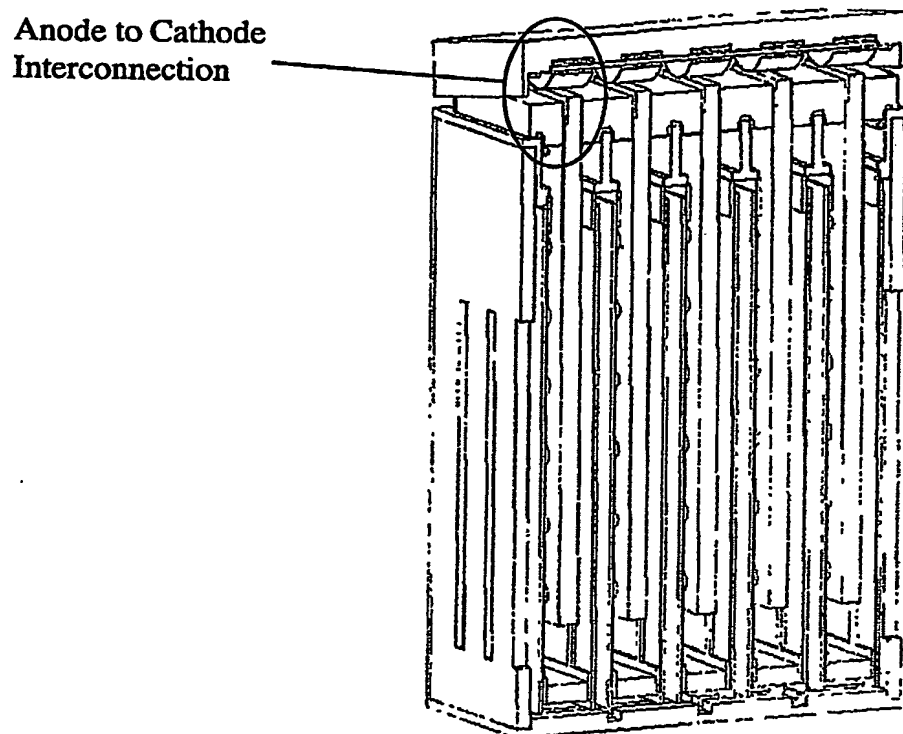
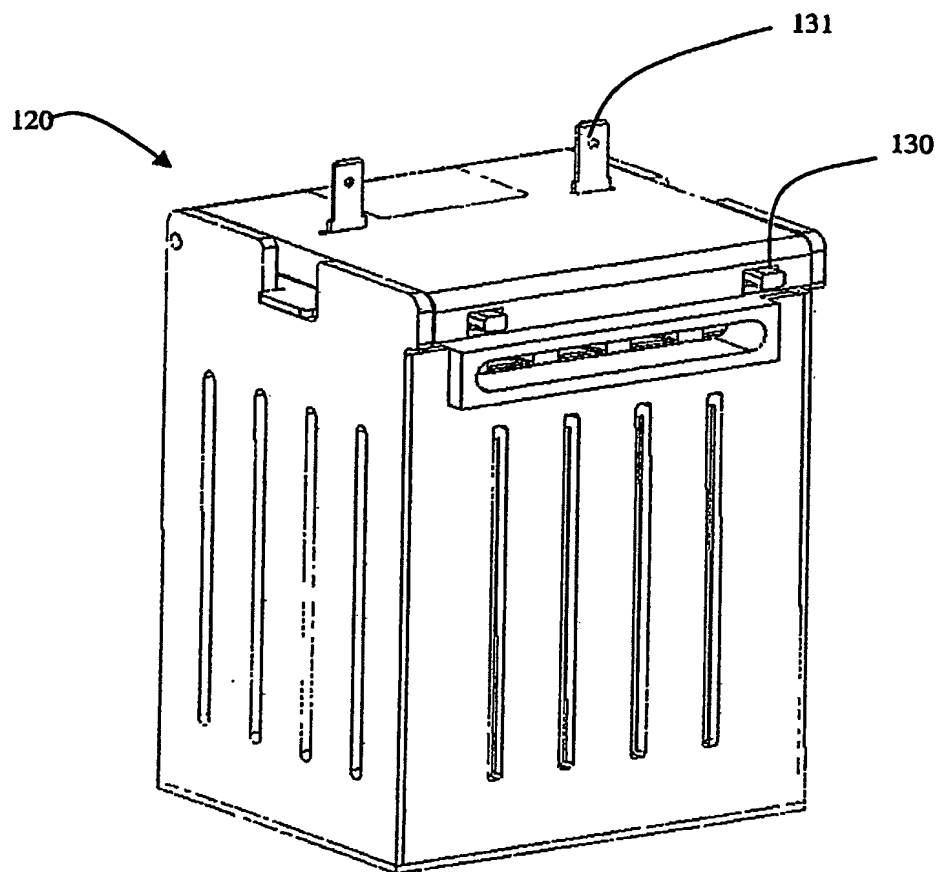
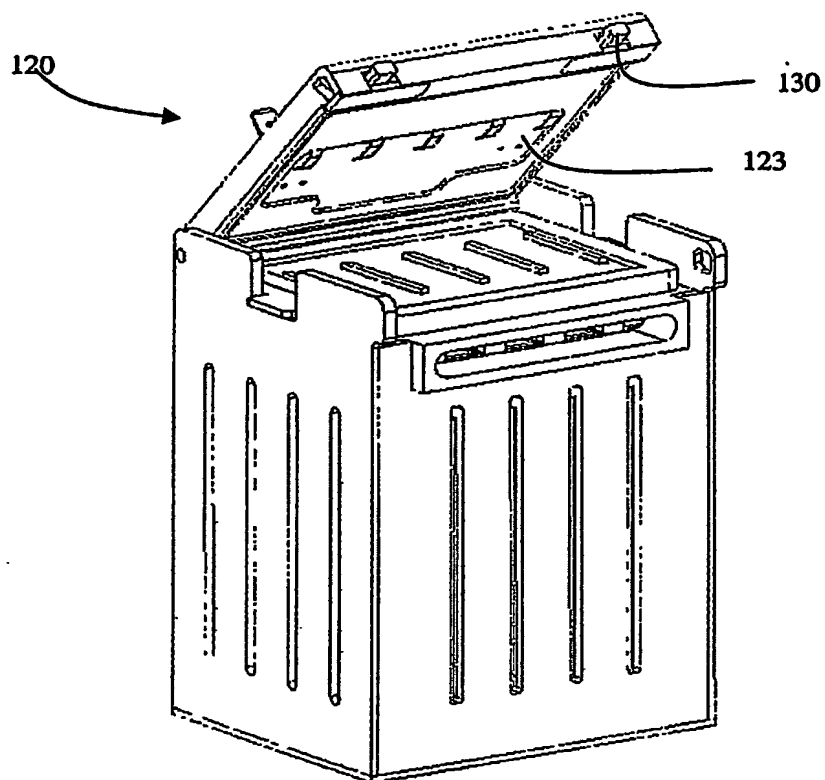


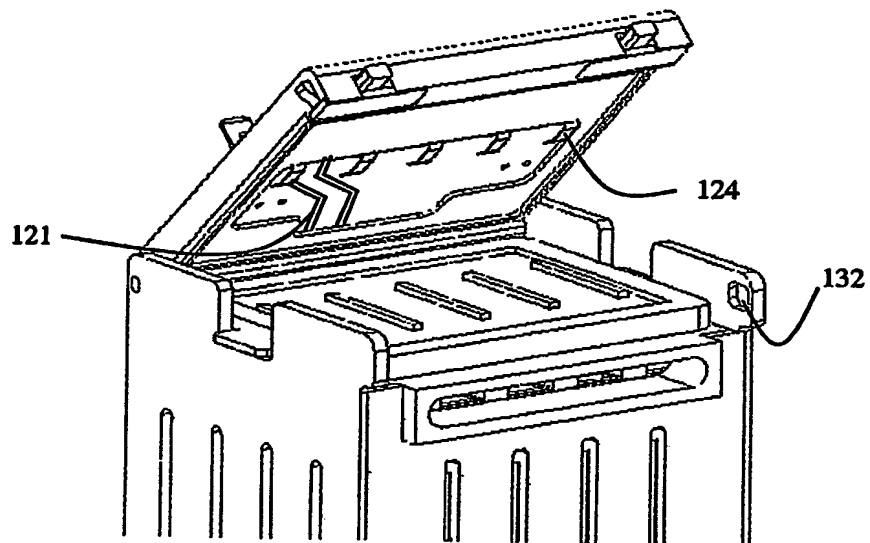
FIGURE 2B

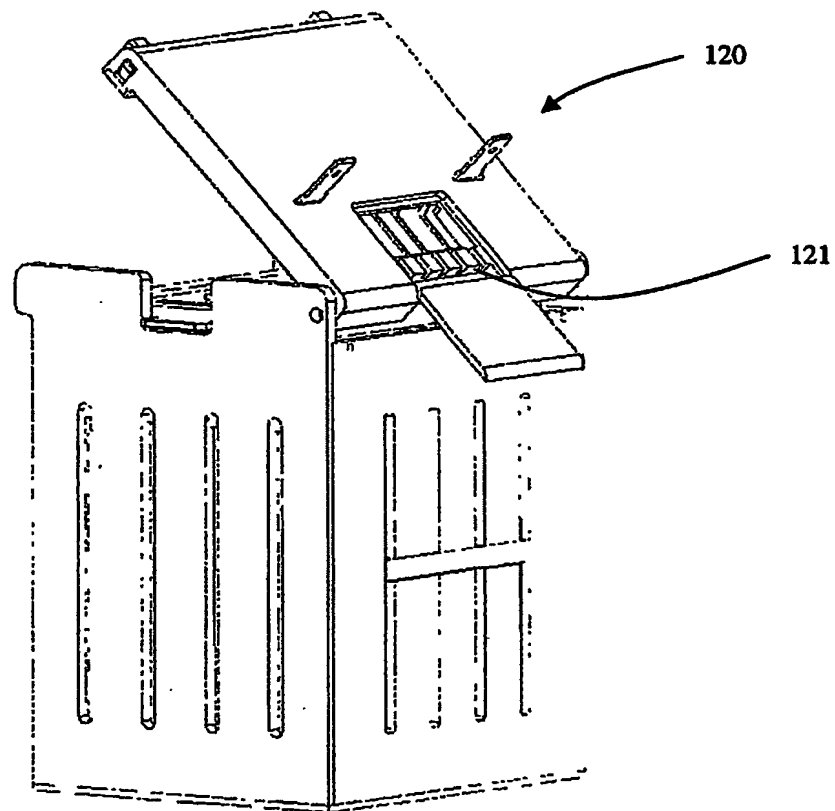
**FIGURE 3**

SUBSTITUTE SHEET (RULE 26)

**FIGURE 4A**

**FIGURE 4B**

**FIGURE 4C**

**FIGURE 4D**